Lake Michigan Mass Balance Project: The QA Process

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LMMB QA & Data Management Peer Review
April 28, 1999

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Great Lakes National Program Office

Chair, Quality Assurance Workgroup

(*since April 1996***)**

Information Management Workgroup

(*since April 1998***)**

The Project

- ❖ Lake Michigan Enhanced Monitoring Program
- ❖ Designed to provide critical input for the Lake Michigan Mass Balance Project

Goal of LMMB

❖ Develop a scientific base of information to guide future Lake Michigan management decisions for toxic contaminant loadings reduction efforts at Federal, State and Local levels

Purpose of LMMB

❖ To model the fate and transport of 4 major contaminants in the Lake Michigan ecosystem:

- PCBs: congener specific
- *trans*-Nonachlor
- Atrazine
- Total Mercury

Components of Ecosystem Measured

- ❖ **Water Column**
  - • **Open Lake and Major Tributaries**
- ❖ **Fish**
  - • **Top predators and Forage Base for Diet Analysis and Contaminant Burden**
- ❖ **Lower Pelagic Foodchain**
  - • **Species Diversity, Taxonomy, and Contaminant Burden**
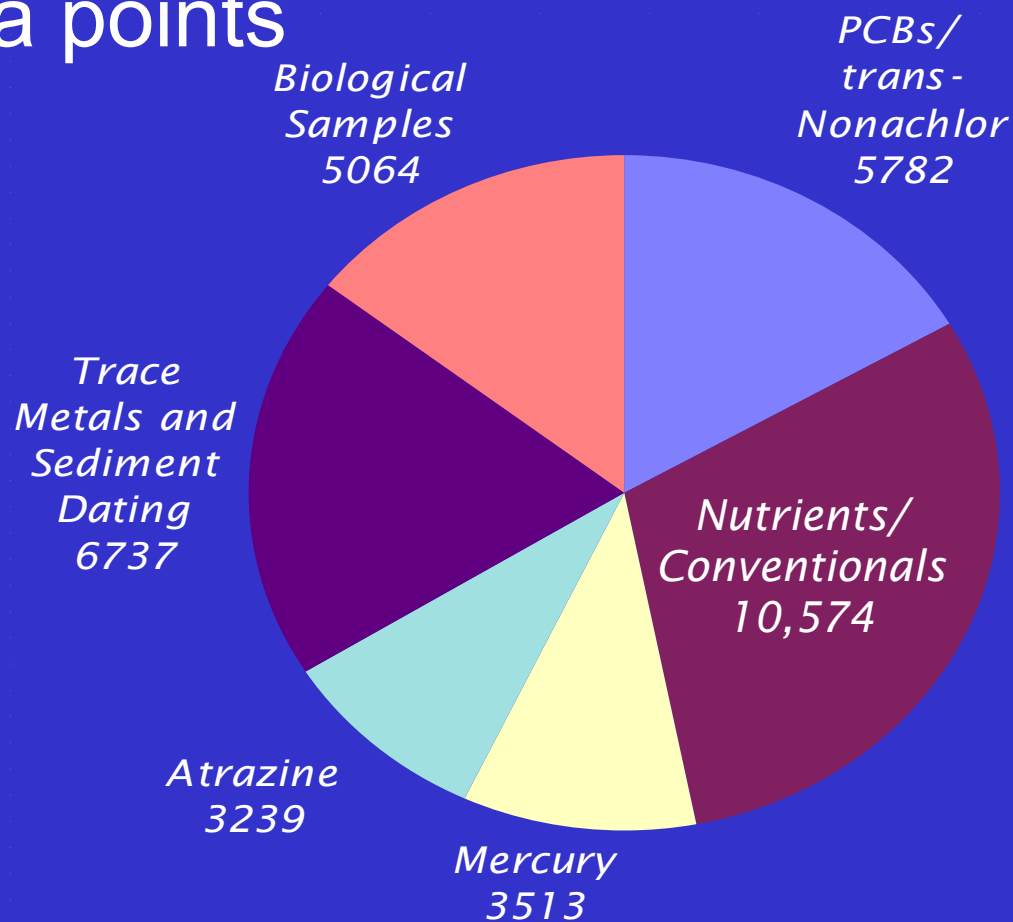- ❖ **Sediments**
  - • **Cores and Burden Traps for Contaminants and Sedimentation Rate**
- ❖ **Atmospheric**
  - • **Wet and Dry Deposition in particulate, vapor, and precipitation**

Total Number of Samples

❖ 38,146 samples with over 1 million result data points

Biological Samples 5064

PCBs/ trans- Nonachlor 5782

Trace Metals and Sediment Dating 6737

Nutrients/ Conventionals 10,574

Atrazine 3239

Mercury 3513

Background

Data Quality Objective session held on December of 1992 with various technical experts and managers:

Conclusions:

Tributary DQO's:

"Estimate 90% of the tributary loads of PCBs to Lake Michigan at +/- 25% at the 95% confidence interval."

Background (*continued*)

AIR DQO's:

"*Estimate atmospheric concentrations of identified parameters for Lake Michigan in a manner that will provide an annual atmospheric loading estimate within +/- 100% at the 95% confidence interval.*"

Background (*continued*)

Model Output Data Quality Objective:

"It is proposed that the model output should be within a factor of 2 of the observed concentrations in the water column and target fish species .... From the Green Bay Mass Balance Study, it is estimated that the required level of model accuracy can be achieved if loadings and contaminant mass in significant environment compartments are determined to within +/- 20 to 30 percent of the actual value."

Lake Michigan Mass Balance Collaborators

❖ **U.S. EPA**

- Great Lakes National Program Office
- Region 5 Water and Air Divisions / Region 2
- Office of Research and Development
  - *Large Lakes Research Station*
  - *RTP*
- Office of Air and Radiation - OAQPS
- Office of Water

Lake Michigan Mass Balance Collaborators

- ❖ United States Geological Survey
  - Biological Research Division (formerly NBS)
  - Water Resources Division
- ❖ U.S. Fish and Wildlife Service
- ❖ U.S. Department of Energy - Battelle NW
- ❖ National Oceanic and Atmospheric Administration
- ❖ Environment Canada
- ❖ Illinois Department of Natural Resources
- ❖ Michigan Department of Environmental Quality
- ❖ Michigan Department of Natural Resources
- ❖ Indiana Department of Environmental Management
- ❖ Wisconsin Department of Natural Resources

LMMB QA/Data Workgroup

Chair, QA Manager - Louis Blume, US EPA GLNPO

QC Coordinators

MERCURY
Kim Conmy
Judy Schofield
DynCorp Inc., Alexandria, VA

**NUTRIENTS/
CONVENTIONALS**
Debra Piper, GRACE Analytical
Chicago, IL

ORGANICS/ATRAZINE
Marcia Kuehl, GRACE Analytical
Chicago, IL

CHEMISTS/SPREADSHEET EXPERTS
Dwayne Holmes
Mike Kvitoud
Renee Morris
Rick Mealy
GRACE Analytical, Chicago, IL

**STATISTICAL SUPPORT/
  METHODS COMPENDIUM**
Judy Schofield
Kim Conmy
Ken Miller, Becky Dohse
Lynn Riddick, DynCorp Inc., Alexandria, VA

RDMQ DEVELOPMENT
Bill Sukloff, Environment Canada

QA/DATA COORDINATOR
Lucy Stanfield
Environmental Careers Organization

LMMB QA/Data Workgroup

Chair, Data Manager – Ken Klewin, US EPA GLNPO

ORACLE DATABASE DEVELOPMENT
Jeff Sabol
Hilary Price
Jamie Sullivan
AMS Inc., Fairfax, VA

OTHER GLENDA DATA PARTICIPANTS
George Mbogo, Database Administrator
Marvin Palmer, Backup DBA
US EPA GLNPO

GLENDA DATA
Upload/Access Coordinator - Post LMMB
Doug Salisbury, Dyncorp Inc., Chicago, IL

LMMB QA Program Motto

"WHATEVER IT TAKES"

"SHARE THE PASSION"

"BABY STEPS"

Key Components of LMMB Quality Management System

❖ Close working relationship between data managers and quality control coordinators

❖ Involved in planning at early stages of process

❖ Investigator defined methods and measurement quality objectives

❖ Utilization of multiple performance evaluation studies

❖ Monthly conference calls for principal investigators, quality control coordinators and data management

Key Components of LMMB Quality Management System

- ❖ Development of a data reporting format and database in advance

- ❖ Use of a SAS-based data verification system (RDMQ)

- ❖ Quality Assurance Program Plan written as overall guide

- ❖ Quality Assurance funded appropriately with a commitment by Management

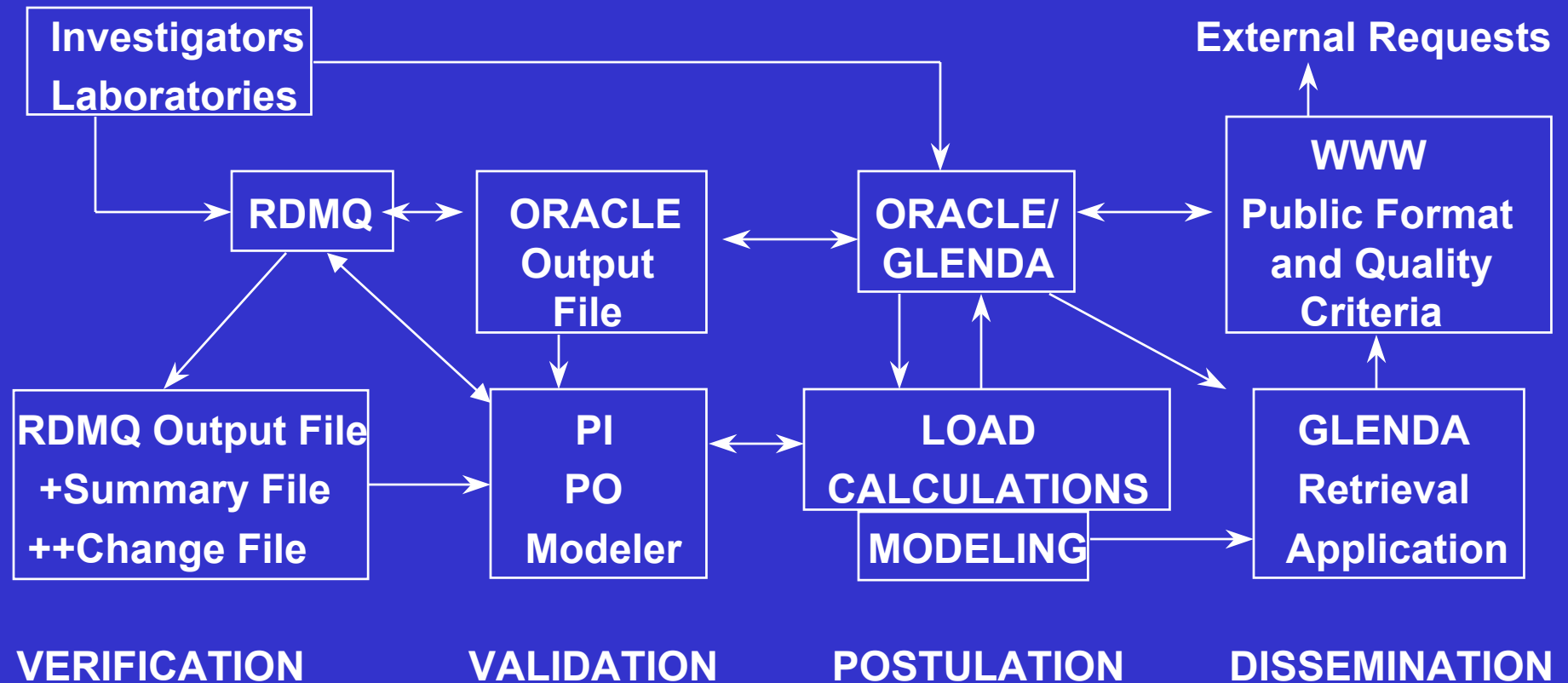- ❖ Quality Assurance Workgroup Chair member of Technical Steering Committee

Performance Based Measurement Approaches

- ❖ In most cases all samples for specific media and analyte groups were analyzed by a single investigator
- ❖ Extremely important to have standard reference materials shared by each investigator

Performance Based Measurement Approaches

- ❖ Communications between investigators through monthly conference calls was critical (i.e. continuous peer review)

- ❖ Important to standardize terminology, reporting codes, comments, formats, and acceptance criteria

Data Flow for LMMB

Investigators Laboratories			**External Requests**
RDMQ	**ORACLE Output File**	**ORACLE/ GLENDA**	**WWW Public Format and Quality Criteria**
RDMQ Output File +Summary File ++Change File	**PI PO Modeler**	**LOAD CALCULATIONS MODELING**	**GLENDA Retrieval Application**
VERIFICATION	**VALIDATION**	**POSTULATION**	**DISSEMINATION**

LMMB Data

37 Focus Groups of LMMB Data

❖ Atrazine - 4

❖ PCB/tNona - 9

❖ Mercury - 7

❖ Nutrients & Conventionals - 11

❖ Biological - 6

Enhanced Monitoring Project - 12

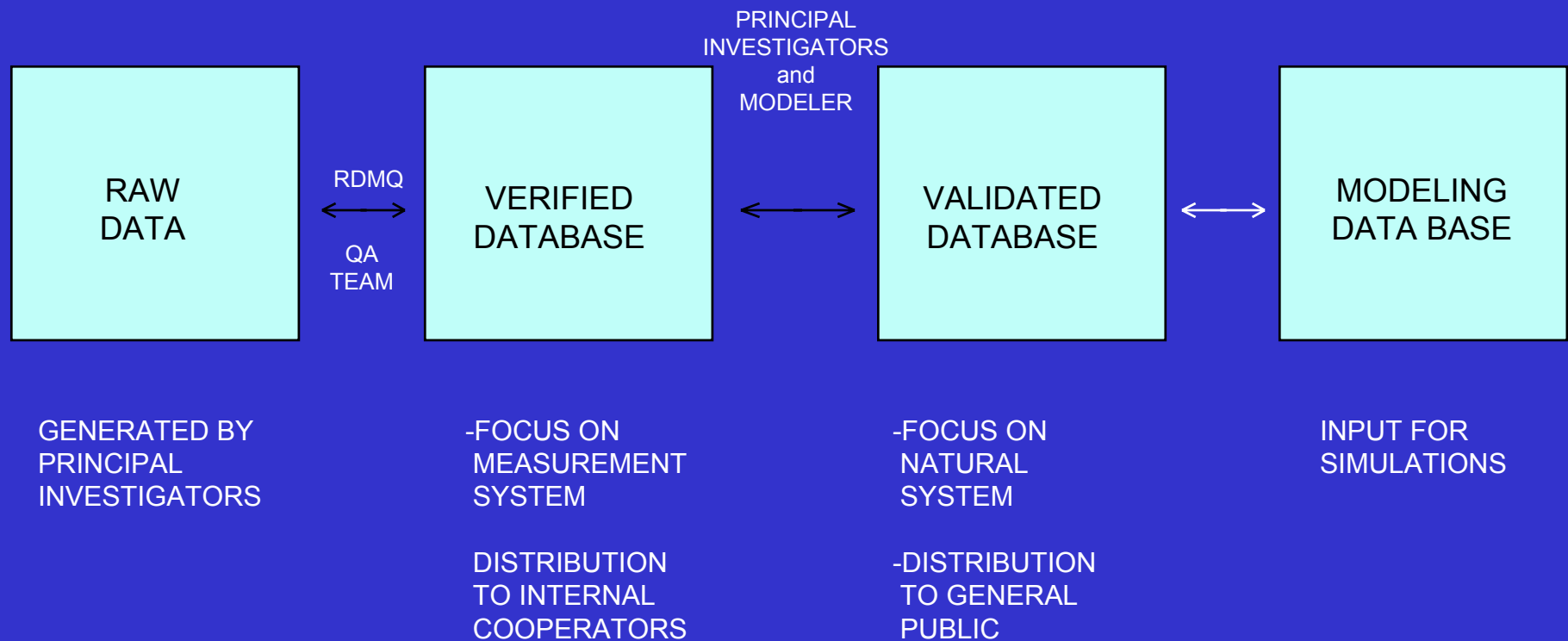Metals - 6

PCBs/PAHs - 6

Verification vs. Validation

Data Verification

process of reviewing data to determine how it compares to **internal measures**

Data Validation

process of reviewing data to determine how it compares to **natural environment**

LMMB Database

RAW DATA		VERIFIED DATABASE		VALIDATED DATABASE		MODELING DATA BASE
	RDMQ ←→ QA TEAM		PRINCIPAL INVESTIGATORS and MODELER ←→		←→	

GENERATED BY PRINCIPAL INVESTIGATORS

-FOCUS ON MEASUREMENT SYSTEM

DISTRIBUTION TO INTERNAL COOPERATORS

-FOCUS ON NATURAL SYSTEM

-DISTRIBUTION TO GENERAL PUBLIC

INPUT FOR SIMULATIONS

General Statistical Approaches

- ❖ Sensitivity
  - Detection Limits (MDLs, DDLs, SDLs)
  - RFS compared to detection limits
- ❖ Precision
  - System - field duplicates
  - Analytical - laboratory duplicates
- ❖ Accuracy
  - System - Field reference samples
  - Analytical - Laboratory reference samples
- ❖ Representativeness, Completeness, Comparability

General Statistical Approaches

❖ Precision can be estimated using duplicate samples.

- Measurement imprecision: field duplicates
- Analytical imprecision: lab duplicates
- Total uncertainty: routine samples

Open Lake Atrazine - Sensitivity

❖ **Analytical Detection Limit**

- Method Detection Limit (MDL) = s*t $_{(0.99, n-1)}$
- Atrazine = 1.26 ng/L
- Deethylatrazine (DEA) = 2.46 ng/L
- 6-Deisopropylatrazine (DIA) = 8.27 ng/L

❖ **System Detection Limit (SDL)**

- SDL = MDL because all field blanks were zero

Open Lake Atrazine - Precision

RPD Between Sample and Field Duplicate Atrazine, Rutgers Lakes
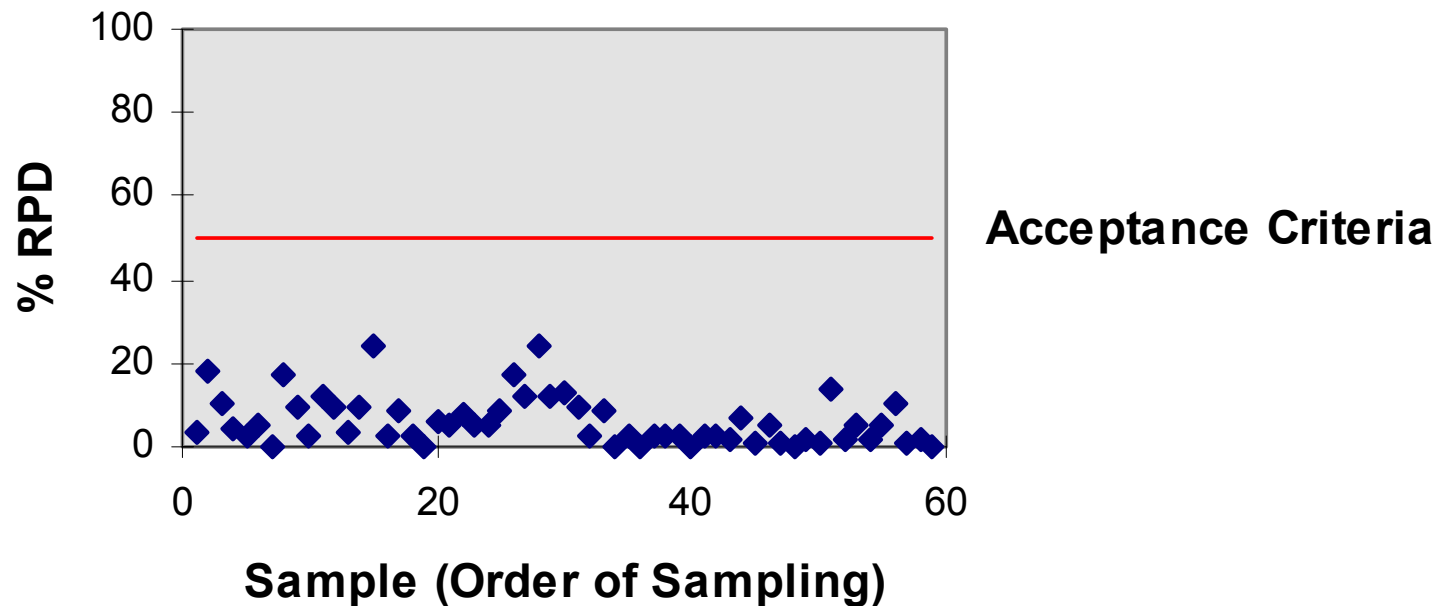
Open Lake Atrazine - Accuracy

**Frequency of Correction Factors
Rutgers Lakes**
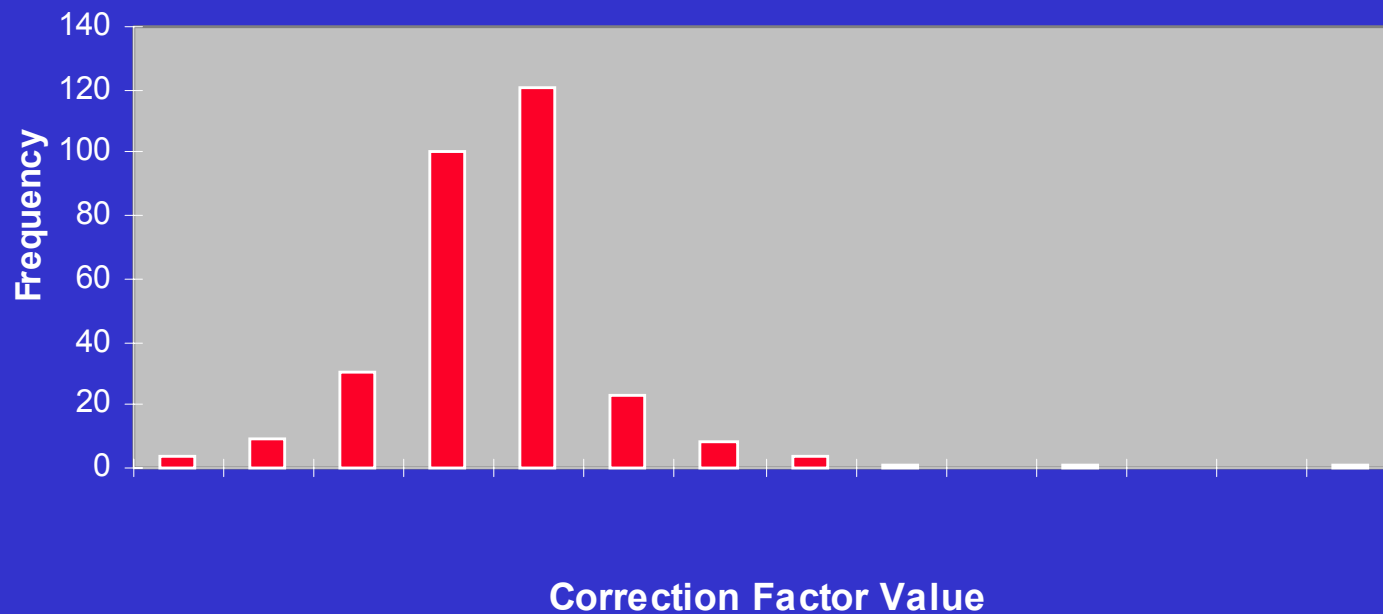
Open Lake Mercury - Sensitivity

❖ **Analytical Detection Limit**

- Daily Detection Limit (DDL) = $s_{(lab\ blanks)} * t_{(0.99,\ n-1)}$
    - DDL_{mean} = 0.063 ng/L
- System Detection Limit (SDL)
    - $SDL_t = s_{(FRBt)} * t_{(0.99,\ n-1)}$ = 0.1971 ng/L

Open Lake Mercury - Sensitivity

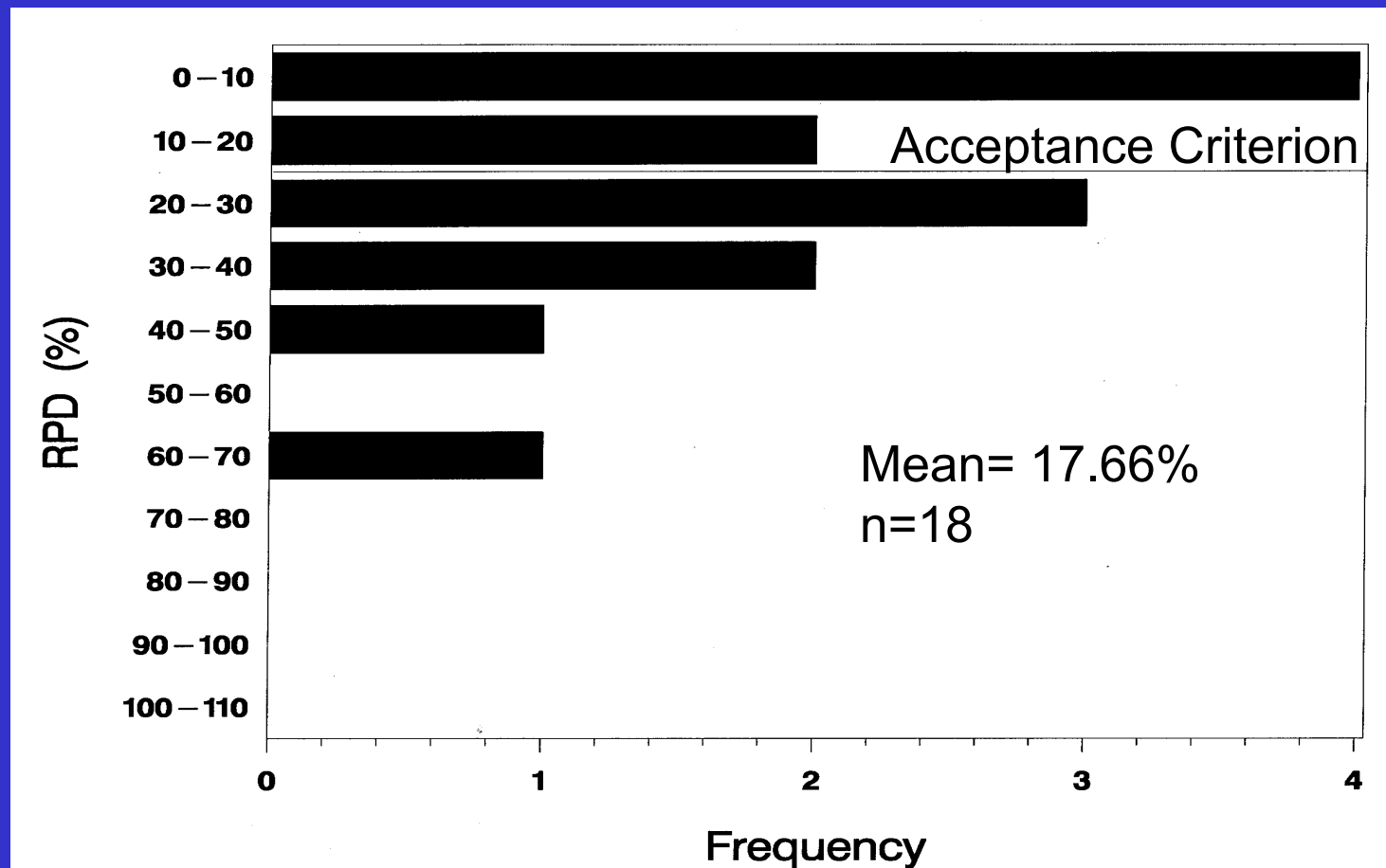## Sample Concentration and DDL By Analytical Time
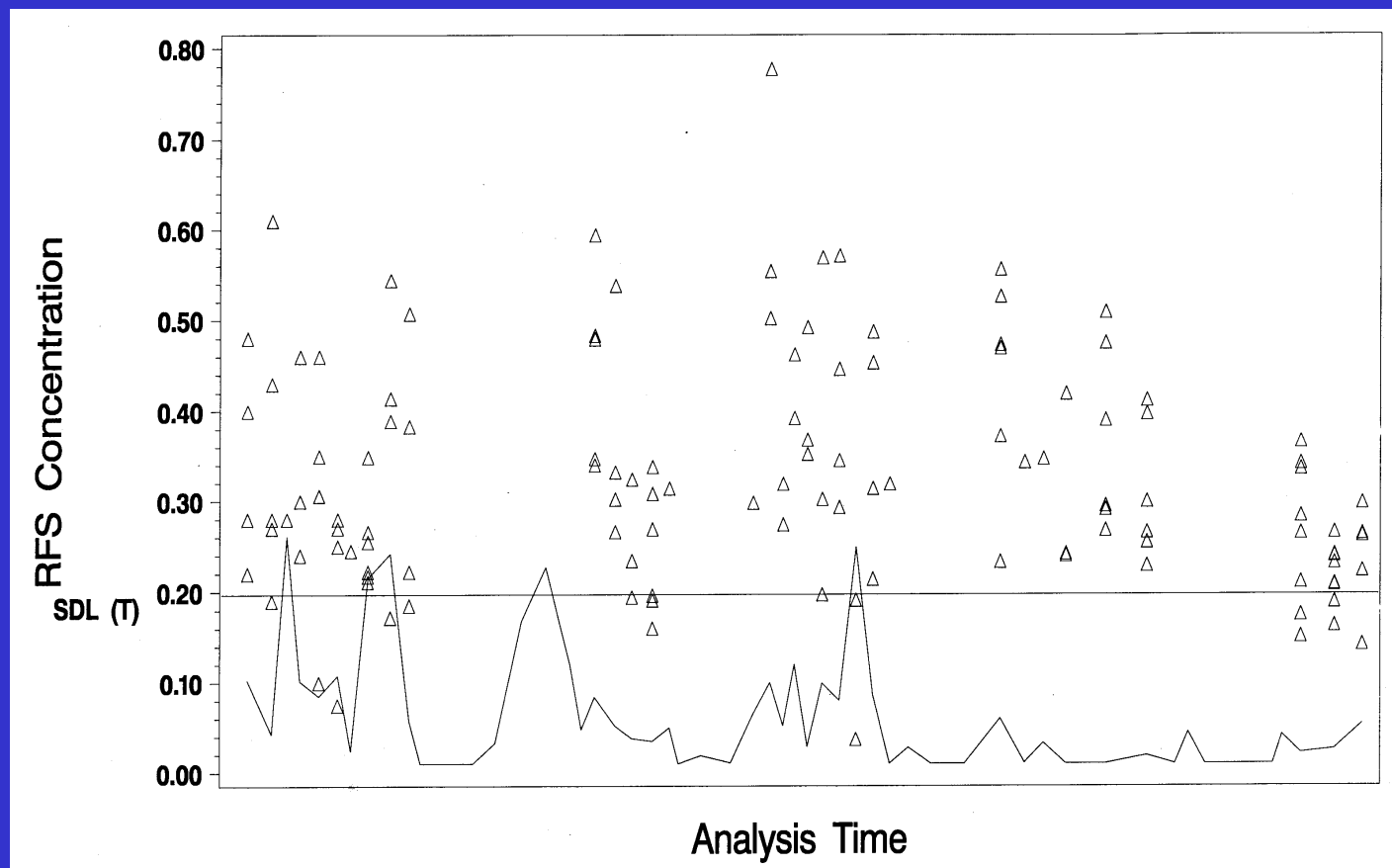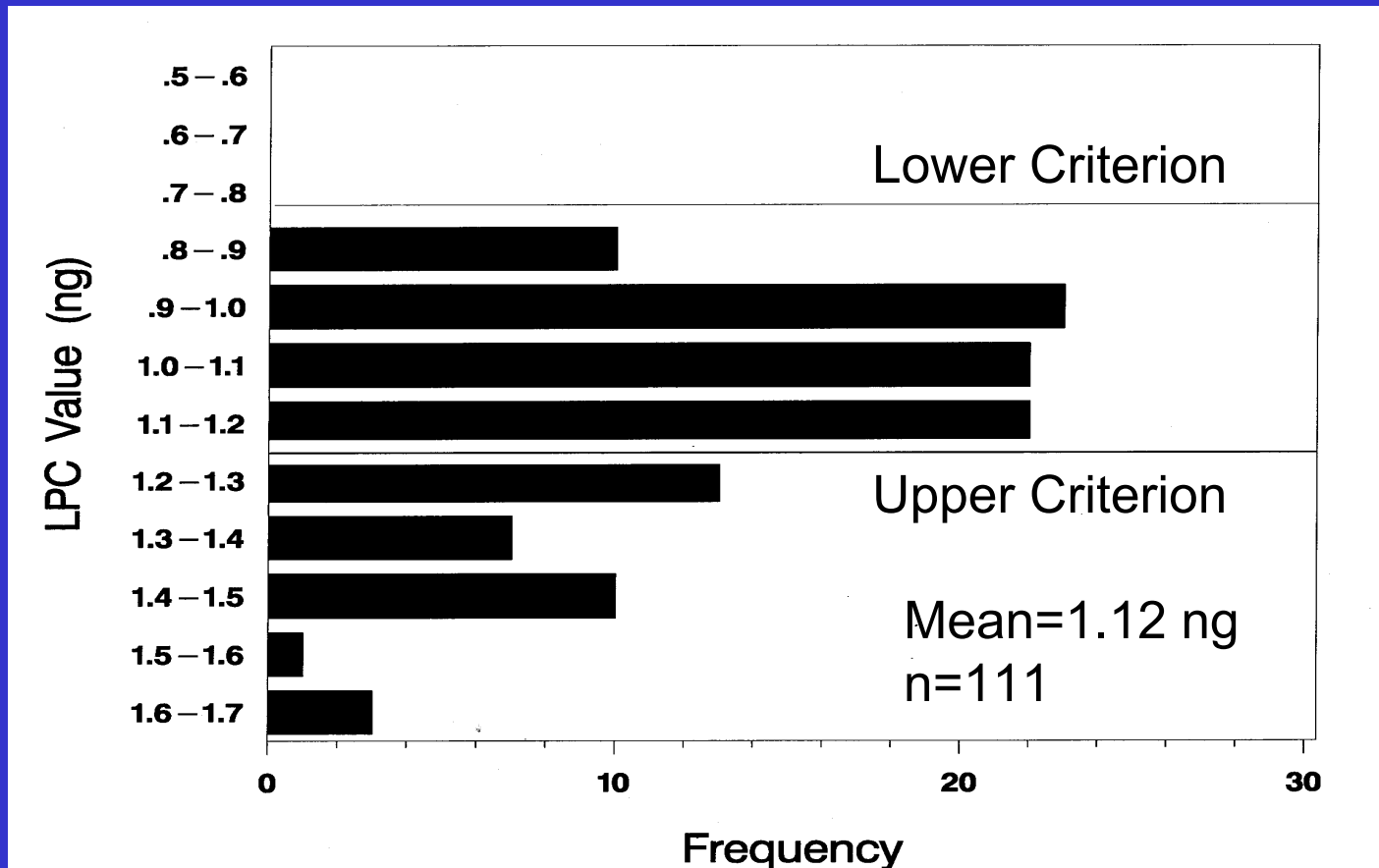
Open Lake Mercury - Precision

Frequency of RPDs Between RFS Samples and Field Duplicates
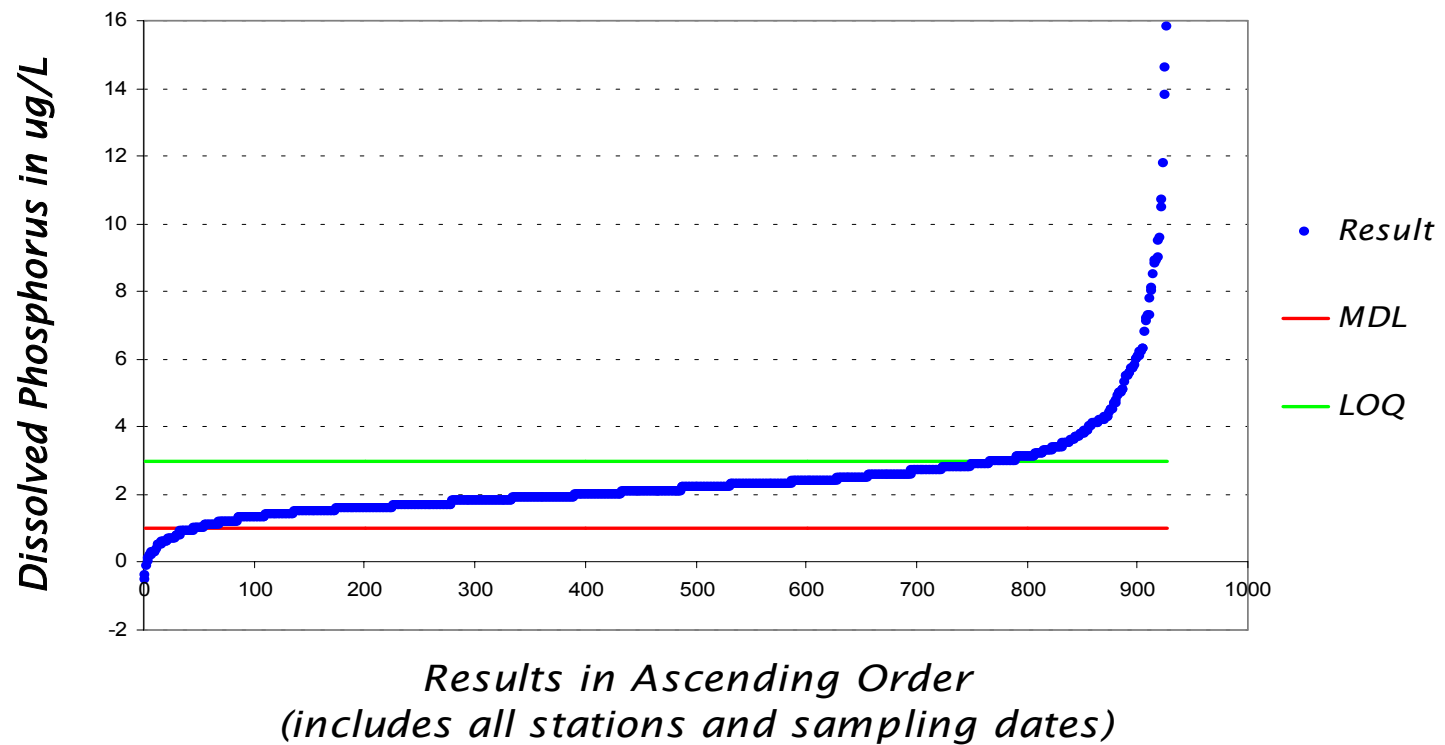
Open Lake Mercury
- Accuracy

Frequency of Lab Performance Checks
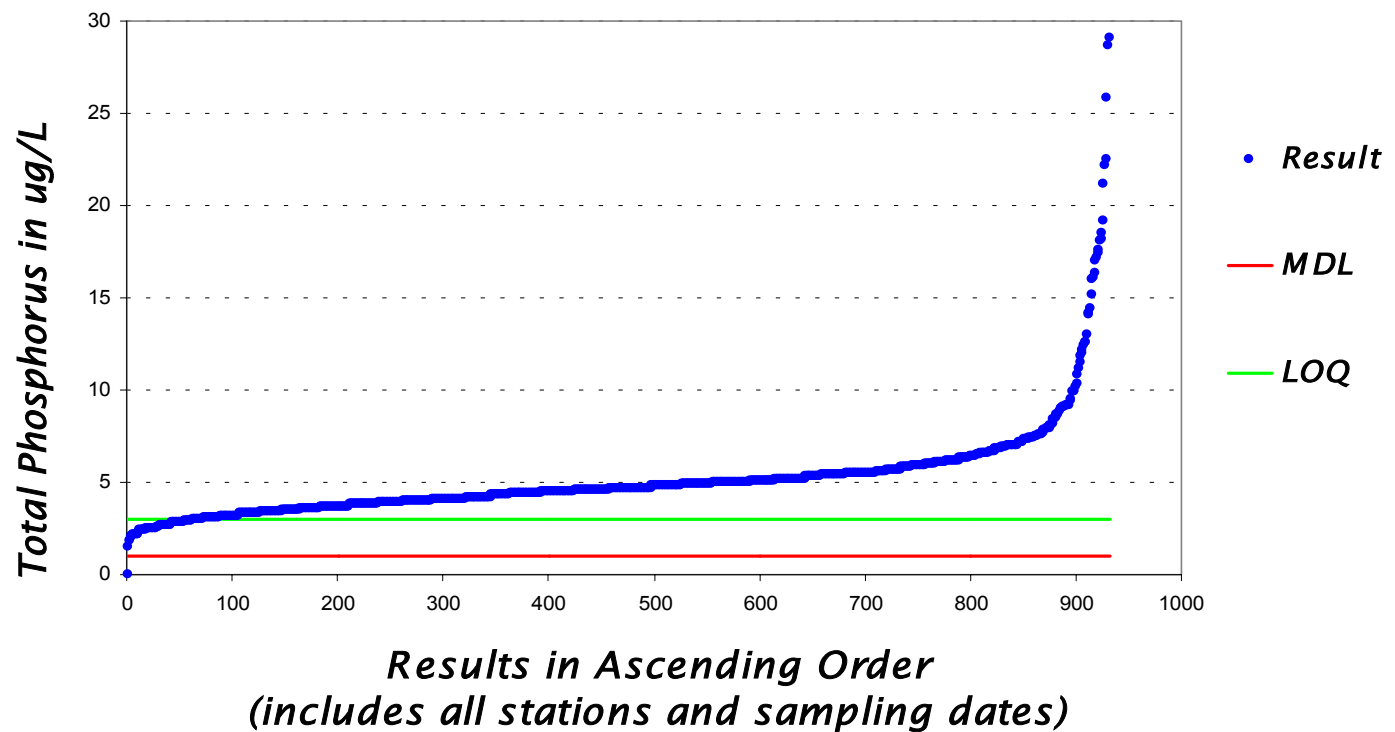
Open Lake Nutrients - Sensitivity

All GRLN Dissolved Phosphorus Results

Results in Ascending Order
(includes all stations and sampling dates)

Open Lake Nutrients
- Sensitivity

Measurement Imprecision

- ❖ Entire measurement system
  - Mean Variance between field duplicates and matching routine samples
- ❖ Analytical measurement system
  - Mean Variance between lab duplicates and matching routine samples

Measurement Imprecision

❖ Estimate proportion of total imprecision due to measurement system using the following ratio:

$$\frac{\text{Mean Variance between samples and field duplicates}}{\text{Variance among all routine samples}}$$

Measurement Imprecision

Open Lake	Percent due to Measurement System
Mercury	27.71%
Phosphorus	5.72%
Atrazine	27.12%

Measurement Imprecision

❖ MDLH

- Imprecision due to Analytical Measurement System: 24.68%

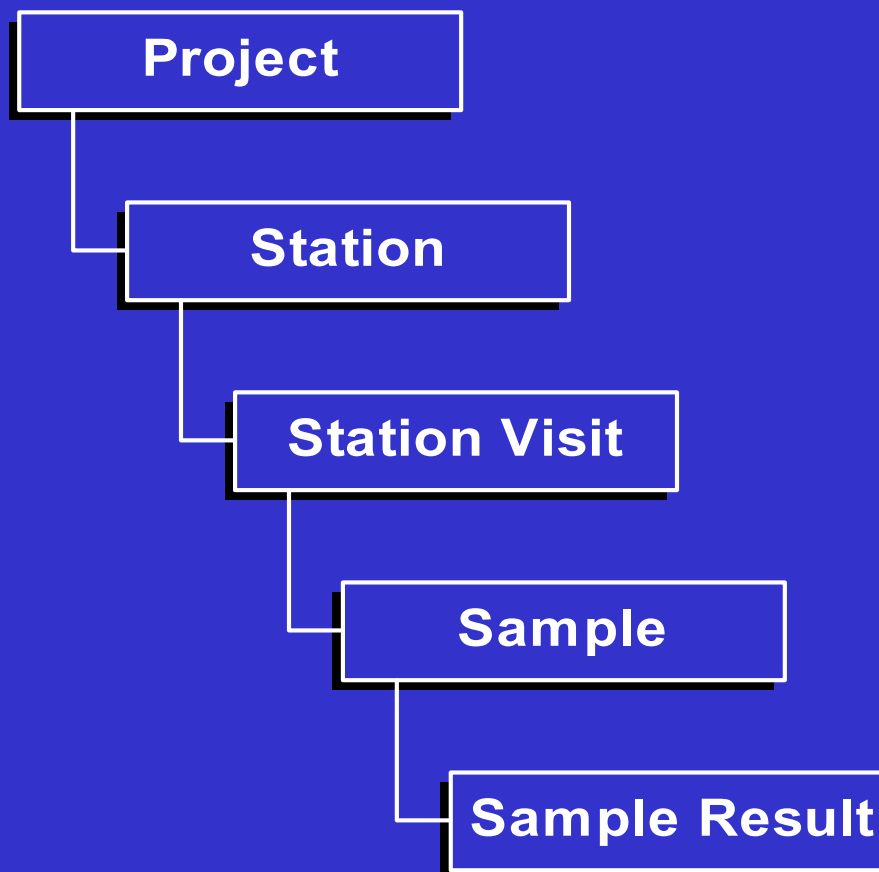- Imprecision due to Entire Measurement System: 27.71%

Great Lakes Database
- A STORET prototype-

- ❖ Shared vision
- ❖ National Environmental monitoring data system
- ❖ Integration: USGS, Drinking Water, etc.

STORET Modernization Contact: Bob King (202) 260-7028

LMMB Database Structure

```
Project
   |
   Station
        |
        Station Visit
             |
             Sample
                  |
                  Sample Result
```

Future Database Directions

❖ Expand database to accommodate other major Great Lakes monitoring programs

❖ Work with States and other interested parties to improve access to Great Lakes environmental monitoring information

Products and Deliverables

❖ QA Program Plans

❖ LMMB Methods Compendium

- *Volume 1 -Sample Collections EPA 905-R-97-012a*
- *Volume 2 -Organic and Mercury Methods, EPA 905-R-97-012b*
- *Volume 3 -Trace Metals, Nutrients, Biology, EPA 905-R-97-012c*

❖ LMMB QA Report

❖ LMMB Data Reports

Products and Deliverables (cont.)

- ❖ Great Lakes Environmental Database (GLENDA)
  - • LMMB Oracle Database (Storet Pilot)
- ❖ Standardized RDMQ Software
- ❖ GLNPO Data Format/QCID's, Remark Codes

Lessons Learned

- ❖ With multiple investigators and multiple methods a <u>sample naming convention</u> should be developed ahead of time to assure uniqueness of sample IDs

- ❖ Develop reporting formats and reference codes prior to start of sample collection

- ❖ Pilot testing of the field, laboratory and data reporting process

- ❖ Development of Quality Assurance Project Plan for models is useful at the earliest stages of the project

LMMB on the Web

☞ **www.epa.gov/glnpo/lmmb/**